

PATENT SPECIFICATION

NO DRAWINGS

1.032.037



Date of Application and filing Complete Specification: Dec. 4, 1962.

No. 45792/62.

Application made in United States of America (No. 161,272) on Dec. 21, 1961.

Complete Specification Published: June 8, 1966.

© Crown Copyright 1966.

Index at acceptance:—O4 X11; D1 P(A6, B2A1, B2A2, B5A, B5B, B5C, C1H1X, C2A12A10, C2B1, C2B2, C2C2, C2C3, C2C4, C2C5, C2C7, C2C8, C2C9, C2C10, C2C11, C2C12, C2C17, C2C18)

Int. Cl.:—C 09 k 3/16 // D 06 m

COMPLETE SPECIFICATION

Spray Compositions

We, GENERAL ANILINE & FILM CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of 111 West 50th Street, New York 20, New York, United States of America, (Assignee of JAMES JOSEPH ROBINSON) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to spray compositions and more especially to self-propelling liquid spray compositions suitable for imparting antistatic properties to materials having a tendency to accumulate a charge of static electricity.

The problem of preventing the accumulation of surface charges on textiles, plastics, leather, rubber, paper, etc., has plagued the industry for many years and a considerable amount of time and effort has been spent in an attempt to obtain a successful solution. There are many compositions suggested in the prior art to be employed as antistatic agents. However, the heretofore employed antistatic agents suffered from many disadvantages including insufficient reduction of static electricity, poor stability over prolonged periods of storage, and the fact that the treated article had antistatic properties for only a comparatively short period of time so that the antistatic treatment had to be renewed after relatively few launderings or dry cleanings.

These problems have been accentuated when attempts have been made to formulate such antistatic agents in the form of the increasingly popular self-propelling liquid spray compositions. Such attempts have for example raised further problems because of inadequate solubility and/or missibility with the liquefied gas propellant, insufficient stability in the pressure container, increased tendencies towards corrosion of the metal pressure

container and metal parts of sprayed articles or metal parts with which the sprayed articles come in contact. Other problems have arisen because of insufficient lubricating and/or anti-wear properties, and increased tendencies of the sprayed articles to accumulate soil. A number of known antistatic agents have limited use because of their toxicity.

It is an object of this invention to provide a self-propelling liquid spray composition which will not be appreciably subject to one or more of the above described disadvantages. Another object of this invention is the provision of such a composition suitable for the treatment of articles to diminish their tendency to accumulate a charge of static electricity.

According to the present invention there is provided a self-propelling liquid spray composition comprising, by weight,

- (1) 20 to 99% of a liquefied gas propellant,
- (2) 0 to 60% of a coupling solvent, and
- (3) 1 to 20% of an organic phosphate ester chosen from the mono-, di- and triesters of phosphoric acid with a nonionic surface active agent, the surface active agent being a condensation product of at least one mole of an alkylene oxide of 2 to 4 carbon atoms inclusive with one mole of a reactive-hydrogen containing compound of at least 6 carbon atoms, the metal, ammonium and organic amine salts of the said mono- and diesters, and mixtures thereof. It has been found that the use of the above defined phosphate esters in such spray compositions enables the attainment of improved and unexpected results with respect to lower toxicity, increased stability in the pressure container, decreased corrosion of metal parts of the pressure container even in the presence of water, improved dispersibility with the liquefied gas propellant, improved lubricant and antistatic properties of sprayed

[P]

therewith, and decreased corrosion of metal parts with which the spray or sprayed articles come in contact.

5 The phosphate esters employed in the present process are known compounds, being derived from known nonionic surface active agents as made for example by reaction of from 1 to 2 up to 150 or more moles of an alkylene oxide of 2 to 4 carbon atoms inclusive with one mole of a compound containing at least 6 carbon atoms and a reactive hydrogen atom.

10 The alkylene oxide employed in the production of the precursor nonionic surface active agents may be propylene oxide, butylene oxide, isopropylene oxide, isobutylene oxide, epichlorhydrin, or preferably ethylene oxide. As compounds to be reacted therewith containing a reactive hydrogen atom there may be mentioned generally saturated or unsaturated, straight or branched, natural or synthetic alcohols such as lauryl alcohol, oleyl alcohol, Oxo tridecyl alcohol, alcohols of the "Pluronic" (trade mark) type, namely polyoxyethylenated derivatives of polymerized propylene and like compounds, or their mono-ether, monoester or other derivatives as disclosed for example in U.S. patent Specification 2,674,619 and the like, phenols such as phenol per se and alkyl phenols including mono-, di-, and tri-butyl-, -nonyl, and -octadecyl-phenol, -cresol and the like, thiols such as dodecyl mercaptan, thiophenol, thionaphthol, benzo-mercaptan and the like, primary and secondary amines such as lauryl amine, stearyl amine, dioctyl amine and the like, and carboxylic and sulfonic acids and their amides such as lauric, oleic, and stearic acid and their amides, dodecyl and dodecyl benzene sulfonic acids and sulfonamides, and the like. The foregoing reactive hydrogen-containing compounds are merely illustrative, a more complete disclosure of such compounds and their condensation products with alkylene oxides suitable for phosphorylation to produce the phosphate esters operative herein appearing for example in U.S. patent Specification 3,004,056 and 3,004,057. Accordingly, such disclosures in the said U.S. patent Specifications, so far as they relate to the production of free mono- and di- acid phosphate esters of nonionic surface active agents the surface active agent being a condensation product of at least one mole of an alkylene oxide of 2 to 4 carbon atoms inclusive with one mole of a compound containing at least 6 carbon atoms and a reactive hydrogen atom, and salts and mixtures thereof, are specifically incorporated herein by reference thereto. Such disclosures include for example column 1, line 43 to column 6, line 41 of U.S. patent Specification 3,004,056 and column 2, line 14 to column 6, line 37 of U.S. patent Specification 3,004,057.

65 While any method may be employed for phosphorylating the above defined nonionic sur-

face active agents, as for example by reaction of such agent with polyphosphoric acid, phosphorous oxychloride, and the like, unexpectedly improved results are obtained when phosphate esters are employed herein as produced by the processes disclosed in the said U.S. patent Specifications 3,004,056 and 3,004,057. The process of U.S. patent Specification 3,004,056 broadly comprises reacting one mole of P_2O_5 with 2 to 4.5 moles of the nonionic surface active agent under substantially anhydrous conditions and at a temperature below about 110° C. down to about room temperature. The process of U.S. patent Specification 3,004,057 is an improvement thereover involving carrying out the aforementioned reaction in the presence of a small amount of a phosphorus-containing compound such as hypophosphorous acid, salts of hypophosphorous acid, phosphorous acid and salts and esters of phosphorous acid, preferably hypophosphorous acid or sodium hypophosphite.

As pointed out in the aforementioned U.S. patent Specifications, the products there produced are complex in nature, generally containing about 20 to 45% of the secondary (mono-acid) phosphate ester, 30 to 80% of the primary (di-acid) phosphate ester, and 0 to 40% of the unreacted nonionic surface active agent. Small amounts of unidentified by-products may also be present. A similar phosphorylating process may be employed in which relatively higher proportions of P_2O_5 are reacted with the nonionic agent, as for example from about 0.5 to 3 moles of P_2O_5 per mole of nonionic agent. Such a process would likewise yield mixtures of mono- and di- acid phosphate esters, though perhaps in different proportions with little or no tertiary phosphate esters.

The above described mono- and di- acid phosphate esters may be employed in the present spray compositions in their free acid form, since it has been found that they inhibit yellowing or discolouration of certain types of textile fibers and other articles particularly modified acrylic fibers. It is generally preferred however, for optimum antistatic, anti-corrosive, antiwear, and/or lubricant properties to employ these phosphate esters in the form of their partially or preferably completely neutralized salts containing as cations metals (including alkali metals, alkaline earth metals and other metals), ammonium and organic amines, as disclosed in column 5, lines 49 to 67 of U.S. patent Specification 3,004,056. Completely neutralized salts having a pH of about 7 to 8 are preferred.

In addition to the salts and cations disclosed in the said U.S. patent Specification, there may also be employed with advantage herein salts of the mono- and di- acid phosphate esters with organic amines referred to as ampholytic compounds. These ampholytic

compounds e.g. sodium - N - methyl tauride, sodium sarcosinate, are well known, being generally organic compounds containing at least one sulfonic, phosphoric, phosphonic, carboxylic or other acid group and at least one basic amino group or the like, whereby the compound can act simultaneously as an acid or a base. By way of illustration only, there may be further mentioned as suitable ampholytic compounds amino carboxylic acids such as ethylenediamine tetraacetic acid, N-hydroxyethyl ethylenediamine triacetic acid, N-triacetic acid, α -aminobutyric acid, gamma-aminobutyric acid, α -aminopentanoic acid, and glycine, and the like, and amino sulfonic acids such as taurine, gamma-aminopropane-sulfonic acid, other α , β , gamma . . . and omega alkane sulfonic acids and the like, and the N-alkyl (methyl, nonyl, octadecyl, etc.), aralkyl (benzyl), and cycloalkyl (cyclohexyl) substituted derivatives of such aminocarboxylic, aminosulfonic, aminophosphoric, and aminophosphonic acids and the like. For neutralization of the above described acid phosphate esters, these ampholytic compounds are employed in the form of their salts (of the acid radicals therein) with cations of the type referred to in the said U.S. patent Specification 3,004,056.

The triesters of phosphoric acid with the defined nonionic surface active agent (tertiary phosphate esters) may also be employed in the present spray compositions although they are less desirable because of the absence therefrom of free acid salt-forming groups (polar groups) considered advisable for antistatic purposes. These triesters may be prepared in known manner by reaction of the nonionic surface active agent with, for example, phosphorous oxychloride, if desired in the presence of an acid-binding agent to neutralize the by-product HCl. Alternatively, the HCl may be removed by blowing, neutralization, or other known expedients. The small amounts of secondary phosphate esters (5—20%) and primary phosphate esters (2—10%) usually produced simultaneously with the tertiary phosphate esters may advantageously be allowed to remain in the mixture or may be removed by treatment with an ion exchange resin or other means.

The liquefied gas propellants operative herein are likewise well known in the art and may be defined as any liquid having a boiling point below atmospheric temperatures at atmospheric pressures. Such liquids, and the present spray compositions containing them, must be maintained in a confined space under pressure (e.g. in a pressurized container of known type) at atmospheric temperatures to prevent boiling, vaporization, or gasification thereof. When these spray compositions are released from the pressurized container through a restricted orifice into the atmosphere, a spray of more or less fine particles or droplets of the composition is formed as a result of the sudden expansion of the liquefied gas propellant. Commonly employed liquid gas propellants operative herein include the chlorofluoro hydrocarbons of the methane and ethane series (a number of these are available under the trademarks "Freon", "Genatron", etc.), methylchloride, dimethylether, propane, butane, isobutane, and the like. Other operative liquefied gas propellants are disclosed in the table in column 3 of U.S. patent Specification 2,524,590, which table is incorporated herein by reference thereto. Mixtures of propellants may also be used.

Depending upon the solubility properties of the chosen phosphate ester or esters and liquefied gas propellant, the spray compositions of the present invention may be in the form of a solution, oil-in-water type emulsion, water-in-oil type emulsion, dispersion, colloidal suspension, or even in stratified layers requiring preliminary shaking or other agitation of the pressurized container containing the composition immediately prior to release through the atmosphere on to the object being sprayed. By suitable choice of the nonionic surface active agent, the proportions of phosphating agent reacted therewith, the method of phosphation, and the like, phosphate esters may be obtained which are soluble in a wide range of organic solvents and/or water. Substantially all the phosphate esters employable in accordance with this invention are sufficiently soluble in the commonly employed propellants such as the "Freons", as for example, difluoro-dichloromethane, to permit preparation of the spray composition in the form of a solution. In the event that the phosphate ester or esters are not sufficiently soluble, amounts of up to 60% by weight of a coupling component, otherwise referred to as a coupler, cosolvent or mutual solvent may be included in the composition, which solvent is soluble in, or in which are soluble, the particular phosphate ester and/or liquefied gas propellant chosen for use. As examples of solvents for phosphate esters herein which may be employed in the present compositions, there may be mentioned such non-polar solvents as mineral oil, kerosene, xylene, benzene, toluene, Stoddard solvent, heptane, high boiling naphthas, and the like, and polar solvents such as perchloroethylene, carbon tetrachloride, chloroform, ethylene glycol, acetone, methyl ethyl ketone, ethanol, isopropanol, amyl alcohol, pine oil, Cellosolves, water, aqueous solutions containing up to 25 to 30% polyphosphates such as sodium tripolyphosphate, and the like. "Cellosolve" is a trade mark. Depending upon the volatility of the coupling solvents, spray compositions may be provided which are quick-drying, slow-drying, or non-drying. Those of the above mentioned solvents for phosphate esters herein which are immiscible with the liquefied gas propellant may

still be included in proportions referred to with respect to the coupling solvent, thereby functioning as extenders, carriers, diluents, bulking agents, or the like. It is accordingly to be understood that such solvents are intended to be included within the meaning of the term "coupling solvent".

As stated above, the phosphate esters employed herein have excellent anti-corrosive properties and accordingly water may be included in the present compositions in any desired amounts, corrosion of the metal parts of the pressure container or of articles sprayed or contacted with the present compositions being substantially reduced or eliminated.

The phosphate esters employed herein have the further advantages of being compatible, with a great many organic and inorganic materials whereby known agents of many different types may be included herein such as for example lubricants, brighteners, indicators, other surface active agents, biocides, pesticides, antiseptics, deodorants, perfumes, dyes, pigments, soaps, oils, film forming agents, glycerine and urea. The described phosphate esters also have excellent emulsifying and dispersing powers whereby their use herein in conjunction with the described solvents, other functional agents and the like is facilitated.

The spray compositions of the present invention may be handled, loaded and dispensed in known manner. They may be previously prepared or they may be prepared in a pressurized dispensing container which may be of the usual aerosol type. They must be handled under pressure and/or under temperatures below the boiling point or vapor pressure of the composition to prevent premature gasification and loss of components. In general, they should be formulated so as to provide in the pressurized dispensing container a pressure ranging from about 5 to 300 p.s.i.g. (lbs. per square inch gauge), depending upon the desired rate, quantity and spray particle size, and the character of the spray composition and/or article being treated. Any suitable dispensing pressure may be obtained in known manner by employing either a single chosen liquefied gas propellant or a mixture of one or more such propellants with one or more relatively less volatile (higher boiling) liquids such as trichloromonofluoromethane or the like.

Any materials or articles may be treated with the spray compositions of the present invention which are prone to accumulate a charge of static electricity. Such materials and articles may for example include textiles, plastics, leather, rubber, paper, and the like.

The compositions are highly advantageous for household use as for example for treatment of rugs, upholstered furniture and the like, the treated materials having a greatly reduced tendency to accumulate a charge of static electricity and, relatively speaking, to become soiled. For industrial use, the compositions are highly advantageous during such operations as twisting, spinning, weaving, knitting and the like. The fiber to be treated may be in any of the usual forms and in natural bulk, interwoven or felted form as for example in the form of staple fiber or continuous filaments in bulk form or in the form of tow, rope, yarns, slubbings, warps, fabrics, felts, and the like, and treated as a wound package, running length, fibrous stock or bulk.

The following examples are only illustrative of certain preferred embodiments of the present invention and are not to be regarded as limitative. For example, the compositions may be prepared in less concentrated form or in much more concentrated form without the use of a coupling solvent or with use of any suitable coupling solvent where desired, as for example by inclusion of from about 10 to 20% or more of alcohol, acetone, or the like.

EXAMPLE 1

Into a pressurized aerosol type dispenser is charged under suitable conditions of temperature and pressure a spray composition consisting of 2 g. of the sodium salts of the essentially mono- and di-acid phosphate esters produced by the reaction of one mole of P_2O_5 with four moles of the condensation product of one molecular equivalent of nonylphenol with six molecular equivalents of ethylene oxide, produced as described in U.S. patent Specification 3,004,057, 64.0 g. of trichloromonofluoromethane and 34 g. of dichlorodifluoromethane. The composition is completely compatible, soluble and sprayable. Samples of fabric as received from the manufacturer are sprayed by holding the pressurized container 12 to 18 inches from the test fabric and spraying to give moderate and uniform coverage of about 0.5 to 1.5% of the phosphate esters O.W.F. (on the weight of the fiber) with a fine, light spray. The anti-static properties of the treated samples and untreated control samples of fabric are evaluated at 50% relative humidity in accordance with the AATCC standard test method 76-1959 "Determination of the Electrical Resistivities of Fabrics". The results of the tests are shown in Table I below. Treated samples placed on the floor and walked on for three days show no more soiling than control samples.

TABLE I

	Resistivity log ohm./sq.	
	Control	Treated Sample
Nylon	14.00	11.79
"Dacron" (polyester)	11.72	11.20
Rayon	11.78	11.20
Acrilan (modified polyacrylic)	14.00	12.47

"Dacron" is a trade mark.

EXAMPLE 2

The procedure of Example 1 is repeated except that instead of the said mixture of phosphate esters there is employed a mixture of essentially the triester of phosphoric acid with the condensation product of one molecular equivalent of lauryl alcohol with four molecular equivalents of ethylene oxide produced by reacting three moles of the said condensation product with one mole of phosphorous oxychloride. Further, the fabrics tested in this example are first scoured with a 1% solution of sodium N-oleoyl-N-methyl tauride to remove the manufacturer's finish. The anti-static properties of the treated samples are disclosed in Table II below. All scoured control samples have a resistivity of 14.00.

EXAMPLE 3

The procedure of Example 2 is repeated

except that the phosphate ester employed is the mixture of sodium salts of the mono- and di- acid phosphate esters produced by reaction of one mole of P_2O_5 with 2.5 moles of the condensation product of one molecular equivalent of oxo tridecyl alcohol (from tetrapropylene) with three molecular equivalents of ethylene oxide. The antistatic properties of the treated samples are shown in Table II below.

EXAMPLE 4

The procedure of Example 2 is repeated except that the phosphate ester employed is the mixture of sodium salts of the mono- and di- acid phosphate esters produced by reaction of one mole of P_2O_5 with 2.7 moles of the condensation product of one molecular equivalent of dinonylphenol with 9 molecular equivalents of ethylene oxide. The antistatic properties of the treated samples are shown in Table II below.

TABLE II

	Example		
	2	3	4
Dacron	10.66	10.06	12.94
Acrilan	11.25	11.00	13.20
Orlon (polyacrylonitrile)	10.94	10.91	12.37
Nylon	11.17	10.03	12.31

"Acrilan" and "Orlon" are trade marks.

The results listed in the above tables show that the samples treated in accordance with this invention have substantially better (lower resistivity) antistatic properties than the untreated controls, it being important to note that the maximum resistivity measured by the sensitive equipment is 14.00 and that a dif-

ference of 0.5 in the measured resistivity is significant.

WHAT WE CLAIM IS:—

1. A self-propelling liquid spray composition comprising, by weight,

(1) 20 to 99% of a liquefied gas propellant,

- (2) 0 to 60% of a coupling solvent, and
 (3) 1 to 20% of an organic phosphate ester chosen from the mono-, di- and triesters of phosphoric acid with a nonionic surface active agent, the surface active agent being a condensation product of at least one mole of an alkylene oxide of 2 to 4 carbon atoms inclusive with one mole of a reactive-hydrogen containing compound of at least 6 carbon atoms, the metal, ammonium and organic amine salts of the said mono- and diesters, and mixtures thereof.
2. A composition as defined in claim 1, wherein the said propellant is difluorodichloromethane.
3. A composition as defined in claim 1 or claim 2, wherein the said coupling component is ethyl alcohol.
4. A composition as defined in claim 1 or claim 2, wherein the said coupling component is acetone.
5. A composition as defined in any preceding claim, containing as the organic phosphate ester a mixture of the said salts of the said mono- and diesters.
6. A composition as defined in any preceding claim, wherein the said reactive-hydrogen containing compound is lauryl alcohol.
7. A composition as defined in any one of claims 1 to 5, wherein the said reactive-hydrogen containing compound is nonyl-phenol.
8. A composition as defined in any one of claims 1 to 5, wherein the said reactive-hydrogen containing compound is dinonyl-phenol.
9. A composition as defined in any one of claims 1 to 5, wherein the said reactive-hydrogen containing compound is tridecyl alcohol derived from tetrapropylene by the Oxo process.
10. A composition as defined in any one of claims 1 to 4, containing as the organic phosphate ester a mixture of salts of the said mono- and diesters with an ampholytic compound.
11. A composition as defined in claim 10, wherein the said ampholytic compound is sodium-N-methyl tauride.
12. A composition as defined in claim 10, wherein the said ampholytic compound is sodium sarcosinate.
13. A composition as defined in any one of claims 1 to 4, containing as the organic phosphate ester the said triester of phosphoric acid.
14. A composition as defined in claim 13, wherein the said reactive-hydrogen-containing compound is lauryl alcohol.
15. A composition as defined in claim 5, wherein the said salts are prepared by reaction of about 2 to 4.5 moles of the said nonionic surface active agent with one mole of P_2O_5 .
16. A composition as defined in any preceding claim, wherein the said alkylene oxide is ethylene oxide.
17. A self-propelling liquid spray composition according to claim 1 substantially as hereinbefore described and exemplified.

MEWBURN ELLIS & CO.,
 Chartered Patent Agents,
 70 & 72 Chancery Lane, London, W.C.2,
 Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press (Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.